

Determining Standard Thermodynamic Properties of the Aqueous Triflate Anion Up to 573 K and 30 MPa

Vladimir Majer^{C, S}, Emilie Pourtier and Karine Ballerat-Busserolles

*Blaise Pascal University Clermont-Ferrand / CNRS, Laboratory Thermodynamics and Molecular Interactions,
UMR 6272, Aubiere, Puy de Dome, France
vladimir.mayer@univ-bpclermont.fr*

Josef Sedlbauer

Technical University of Liberec, Department of Chemistry, Liberec, Czech Republic

The trifluoromethanesulfonate (triflate) salts are useful for high temperature studies of aqueous cations of higher valence, such as lanthanides, that tend to ion pair at conditions where the dielectric constant of water considerably decreases. In this context it is necessary to know the standard thermodynamic properties of the triflate ion in order to calculate those of a given cation. The standard molar volumes and heat capacities of aqueous triflic acid and sodium triflate were determined by extrapolating to infinite dilution measurements by vibration tube densitometry and the Picker type flow differential calorimetry over an extended range of temperatures (up to 573 K) and pressures (to 30 MPa). Since the standard thermodynamic properties of Na cation, obtained from NaCl(aq) data, are tabulated, it is possible to calculate the ionic values for the triflate anion that should be in principle identical, within experimental errors, with those for the triflic acid (zero convention for H⁺ adopted). The important differences were, however, observed at temperatures above 473 K. This must be linked with high temperature association of HCl whose properties are generally assimilated to those of the chloride anion and possibly partly also with the association of triflic acid. The possibilities of reconciling the standard thermodynamic data for these aqueous species are discussed in the contribution.